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Novel Synthesis of New 1,2,4-Trithioles by Reductive Coupling of Benzoyldithioacetic Acid Derivatives Mediated by SmI_2

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ABSTRACT: *1,2,4-trithioles* **2a–e** *are readily obtained in good yields by dimerization of benzoyldithioacetic acid derivatives using samarium diiodide as a promotor under very mild conditions. The structures of compounds* **2a–e** *were determined by IR, ^1H, and ^{13}C NMR spectroscopies using heteronuclear multiple bond correlation, heteronuclear multiple quantum correlation, and nuclear Overhauser enhancement spectroscopy experiments, mass spectrometry, and, in the case of* **2a,** *the structure was confirmed by single-crystal X-ray diffraction studies.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:329–335, 2000

INTRODUCTION

Much interest is currently focused on new methods for the synthesis of sulfur-containing compounds, based on their importance in synthetic organic chemistry, their potential bioactivity, and the ever-increasing demand for functionalized molecules in the synthesis of transition metal complexes in organometallic chemistry [1]. The cyclic derivatives of 1,2,4-trithioles are compounds that, due to their structural arrangement, can accommodate a wide-range assortment of potential ligands [2]. The title compounds are commonly synthesized by treatment of carbonyl compounds containing active methylene groups with carbon disulfide in basic media [3]. Others approaches involve, inter alia, oxidation of monoanions of alkanedithioic acids with hypervalent iodine compounds [4], and the photolysis of 1,2-dithiole-3-thiones [5].

In this regard, we have recently reported the preparation of several sulfur derivatives, such as 1,2,4-trithioles, 1,2-dithiole-3-thiones, 1,3-dithiole-4-thiones, 1,3-dithiin-4-thiones, and dixanthates by reaction of aliphatic cyclic ketones with carbon disulfide under basic conditions, followed by an acidic workup [6]. Also, building on the success achieved by varying the functional groups attached to α,β-unsaturated ketones, we extended our studies to include the dithiol group β-positioned on α,β-unsaturated carbonyl compounds, and we succeeded in the

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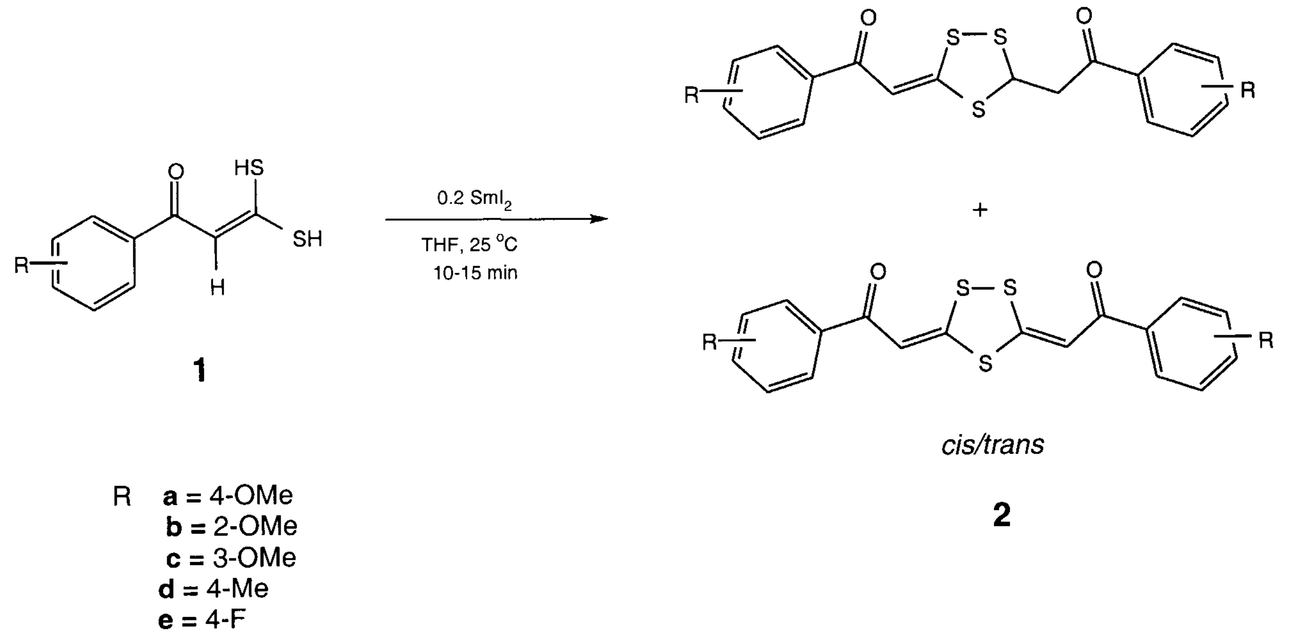
preparation of new dinuclear Fe(0) complexes derived from *para*-substituted derivatives of benzoyldithioacetic acid; these displayed a σ-S coordination instead of the usual η^2 or η^4 π-coordination upon the α,β-unsaturated system of the ligands [7]. On the other hand, in a previous work, we have shown that samarium diiodide is a useful reagent for cyclo- and hydrodimerization of cyclic and noncyclic α,β-unsaturated ketones under neutral and mild conditions, two-mole equivalents of SmI_2 per mole of starting substrate being utilized [8].

Therefore, considering the ease and effectiveness of SmI_2 in such reactions and keeping in mind the synthesis of functionalized ligands derived from benzoyldithioacetic acid derivatives **1a–e,** the use at the reductive coupling mediated by samarium diiodide in either catalytic or stoichiometric amounts was considered. Here we wish to report our findings on such matters (Scheme 1).

RESULTS AND DISCUSSION

As can be seen in Scheme 1, the reductive coupling of benzoyldithioacetic acid derivatives mediated by SmI_2 gives rise to the formation of the 1,2,4-trithiole isomers, namely the *s-cis*, *s-trans*, and the monosaturated coupling product of the two tautomeric entities. Such compounds were found in a 2:2:1 ratio, respectively. The interconversion of *s-trans* to *s-cis* isomers of 1,2,4-trithioles in solution has been documented by use of NMR spectroscopy [9], but, to our knowledge, there are no reports involving the isolation of both isomers.

The structures of compounds **2a–e** were determined by IR, ^{1}H, and ^{13}C NMR spectroscopies and mass spectrometry. IR spectra consistently exhibited, in all cases, absorption bands in the range 1667–1570 cm^{-1} assigned to α,β-unsaturated carbonyl groups with adjacent sulfur atoms, as previously reported in the literature [10]. Mass spectra also showed. In all cases, the peaks corresponding to the expected molecular weight for each proposed structure (the trithiole structure) and very similar fragmentation patterns. On the other hand, ^{1}H and ^{13}C NMR spectra along with heteronuclear multiple bond correlation (HMBC), HMQC, and nuclear Overhauser enhancement spectroscopy (NOESY) experiments allowed the structural assignment for each of the *s-cis* and *s-trans* isomers. Thus, for example, in the case of **2b**-*cis* and **2b**-*trans* isomers, isolated as yellow solids in 40% and 43% yields, respectively, the ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2b**-*cis* showed a singlet at δ 3.92 ppm integrating for 6H, multiplets at δ 6.98 (dd), 7.05 (ddd) and 7.86 (dd) ppm for an ABXY system of aromatic protons and finally a singlet at δ 7.6 ppm (2H) assigned to the vinylic protons. The isomer, **2b**-*trans*, on the other hand, displayed in its ^{1}H NMR spectrum (500 MHz, $CDCl_3$) two sets of signals: two singlets at δ 7.57 and 7.87 ppm that were attributed to the vinylic protons, and at the region of aromatic protons, four sets of duplicated multiplets can clearly be seen at δ 7.91,



SCHEME 1

7.48, 7.05, and 6.99, and 7.82, 7.48, 7.05, and 6.99; this can be inferred as strong evidence for an *s-trans* isomer due to the lack of a plane of symmetry in the molecule. ^{13}C NMR data also support the structural assignment for the *s-trans* isomer, which was corroborated by HMBC, HMQC, and NOESY experiments (Table 1).

In the case of the monosaturated compound **2a**, the structure was confirmed by a single-crystal X-ray diffraction analysis (Figure 1). Cremer and Pople [11] puckering parameters; $Q(2) = 0.619$ Å, $\phi(2) = 154.21°$ show that the 1,2,4-trithiolane ring adopts a twisted conformation with a pseudo C_2 symmetry axis passing through the C3 carbon atom. The 4-methoxybenzoylmethylene and the 4-methoxybenzoylmethyl moieties are essentially planar and display a dihedral angle of 65.36° between them. The α,β-unsaturated carbonyl moiety with an *s-cis* conformation has a *cis* conformation with respect to the disulfide moiety, giving rise to one of the shortest S ⋯ O contacts found in this type of compounds. As a first thought, the lengthening of the C7 = O1 and the S1–S2 bonds could account for a strong S ⋯ O interaction; however, the bond length and the dihedral angle C5–S1–S2–C3 (Table 4) fits very well with Hordvik's curve [12], indicating that the disulfide

TABLE 1 ^{13}C NMR Chemical Shifts for **2b**-*cis* and **2b**-*trans* Isomers

2b-*cis isomer*		**2b**-*trans isomer*	
Carbon	δ	*Carbon*	δ
C_{14}	55.7	$C_{23}C_{14}$	55.7, 55.6
C_{12}	111.7	$C_{12}C_{19}$	111.7, 111.7
C_6	112.7	C_8C_{15}	113.1, 114.6
C_{10}	121.0	$C_{10}C_{21}$	120.9, 121.0
C_8	126.6	C_8C_{17}	125.4, 127.4
C_9	131.5	$C_{22}C_9$	131.4, 131.6
C_{11}	133.7	$C_{11}C_{21}$	133.6, 134.0
C_{13}	158.4	$C_{18}C_{13}$	158.4, 158.7
$C_{3.5}$	158.7	C_5C_3	157.4, 168.6
C_7	185.1	$C_{16}C_7$	185.1, 185.3

TABLE 2 Crystallographic Data for **2a**

Formula	$C_{20}H_{18}O_4S_3$
f.w.	418.52
a, Å	8.535(2)
b, Å	5.462(1)
c, Å	40.658(1)
β, (°)	90.59(3)
V, (Å^3)	1895.3(7)
Z	4
F(000)	872
Crystal system	Monoclinic
Space group	$P2_1/c$
T (°C)	20
2θ range (°)	$3.00 \leq 2\theta \leq 113.0$
ρ_{calc} (g/cm^3)	1.467
Reflections Measured	5370
Unique data	2508
μ (mm^{-1})	3.79
Crystal Size (mm)	0.24 × 0.20 × 0.02
Min, max transmission	0.5279, 0.9229
$wR(F^2)^a$	0.1113
$R(F)^b$	0.0569
Goodness of fit, S^c	0.999
Parameters	245
Min, max peaks, (e/Å^3)	−0.292, 0.252

$^aR = \|Fo| - |Fc\|/|Fo|$.
$^bwR = \{[w(Fo^2 - Fc^2)^2]/w(Fo^2)^2\}^{1/2}$.
$^cS = \{[w(Fo^2 - Fc^2)^2]/(n - p)\}^{1/2}$, where n = number of reflections; p = number of parameters refined.

TABLE 3 Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **2a**

Atom	*x*	*y*	*z*	*Ueq*
S(1)	0.1244(2)	0.0936(4)	0.0322(1)	0.061(1)
S(2)	0.2317(2)	0.0514(3)	0.0780(1)	0.060(1)
C(3)	0.3421(7)	0.3243(12)	0.0781(2)	0.047(2)
S(4)	0.3387(2)	0.4965(3)	0.0417(1)	0.056(1)
C(5)	0.2875(7)	0.2497(11)	0.0134(2)	0.046(2)
C(6)	0.4272(7)	0.3924(12)	0.1046(2)	0.052(2)
C(7)	0.4259(7)	0.2458(13)	0.1335(2)	0.053(2)
O(1)	0.3497(6)	0.0497(10)	0.1336(1)	0.074(2)
C(8)	0.5154(7)	0.3096(12)	0.1637(2)	0.049(2)
C(9)	0.6124(7)	0.5149(13)	0.1662(2)	0.056(2)
C(10)	0.6992(8)	0.5649(14)	0.1946(2)	0.064(2)
C(11)	0.6859(7)	0.4099(12)	0.2215(2)	0.051(2)
C(12)	0.5870(8)	0.2090(13)	0.2195(2)	0.062(2)
C(13)	0.5033(8)	0.1601(14)	0.1909(2)	0.061(2)
O(2)	0.7668(5)	0.4354(10)	0.2502(1)	0.070(1)
C(14)	0.8646(8)	0.6453(15)	0.2542(2)	0.078(2)
C(15)	0.2434(7)	0.3415(12)	−0.0202(2)	0.051(2)
C(16)	0.2596(7)	0.1428(13)	−0.0466(2)	0.051(2)
O(3)	0.3397(6)	−0.0355(10)	−0.0404(1)	0.075(2)
C(17)	0.1823(7)	0.1763(12)	−0.0789(2)	0.047(2)
C(18)	0.0816(7)	0.3694(12)	−0.0863(2)	0.051(2)
C(19)	0.0060(7)	0.3851(13)	−0.1164(2)	0.053(2)
C(20)	0.0295(7)	0.2038(13)	−0.1396(2)	0.049(2)
C(21)	0.1304(7)	0.0103(13)	−0.1333(2)	0.054(2)
C(22)	0.2061(7)	−0.0009(12)	−0.1029(2)	0.050(2)
O(4)	−0.0404(5)	0.1974(9)	−0.1700(1)	0.060(1)
C(23)	−0.1620(8)	0.3715(14)	−0.1761(2)	0.070(2)

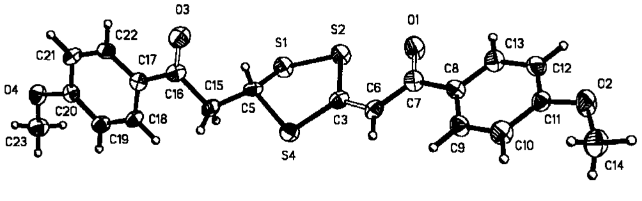


FIGURE 1

TABLE 4 Selected Geometric Parameters for **2a**

Bond Lengths (Å)			
S(1)-C(5)	1.807(6)	C(6)-C(7)	1.422(9)
S(1)-S(2)	2.080(2)	C(7)-O(1)	1.253(7)
S(2)-C(3)	1.763(6)	C(7)-C(8)	1.479(9)
S(1)...O(3)	3.563(5)	C(15)-C(16)	1.533(9)
S(2)...O(1)	2.467(5)	C(16)-O(3)	1.214(8)
C(3)-C(6)	1.348(8)	C(16)-C(17)	1.475(8)
C(3)-S(4)	1.750(7)	S(1)...S(1)[a]	3.505(3)
S(4)-C(5)	1.823(6)	S(2)...S(4)[b]	3.495(3)
C(5)-C(15)	1.500(8)		

Bond angles (°)	
C(5)-S(1)-S(2)	95.5(2)
C(3)-S(2)-S(1)	97.9(2)
C(6)-C(3)-S(4)	122.1(5)
C(6)-C(3)-S(2)	121.2(5)
S(4)-C(3)-S(2)	116.7(3)
C(3)-S(4)-C(5)	97.9(3)
C(15)-C(5)-S(1)	110.8(4)
C(15)-C(5)-S(4)	112.6(4)
S(1)-C(5)-S(4)	105.3(3)
C(3)-C(6)-C(7)	119.9(6)
O(1)-C(7)-C(6)	119.5(6)
O(1)-C(7)-C(8)	117.5(6)
C(6)-C(7)-C(8)	122.9(6)
C(5)-C(15)-C(16)	112.2(5)
O(3)-C(16)-C(17)	121.9(6)
O(3)-C(16)-C(15)	118.6(6)
C(17)-C(16)-C(15)	119.5(6)
S2-C3-C6-C7	−1.5(9)
S1-C5-C15-C16	−83.5(6)
C5-S1-S2-C3	33.2(3)
C3-C6-C7-O1	2.5(10)

[a] Symmetry transformations used to generate equivalent atoms: −x, −y, −z

[b] x, y-1, z.

bond is not affected by any possible interaction between the sulfur atom and the closely adjacent keto oxygen atom.

A pathway that would account for the formation of trithioles **2a–e** is suggested in Scheme 2.

As can be seen, pathway B leads to the formation of compound VI via the reductive coupling of the radical III with a molecule of II giving rise to the intermediate IV, and a subsequent proton transfer leads to cyclization to the trithiole VI. On the other hand, in pathway A, the coupling occurs between the radical III and the tautomer I generating the disulfide VII, and as in pathway B, the proton transfer within such an entity leads to the cyclization process.

CONCLUSION

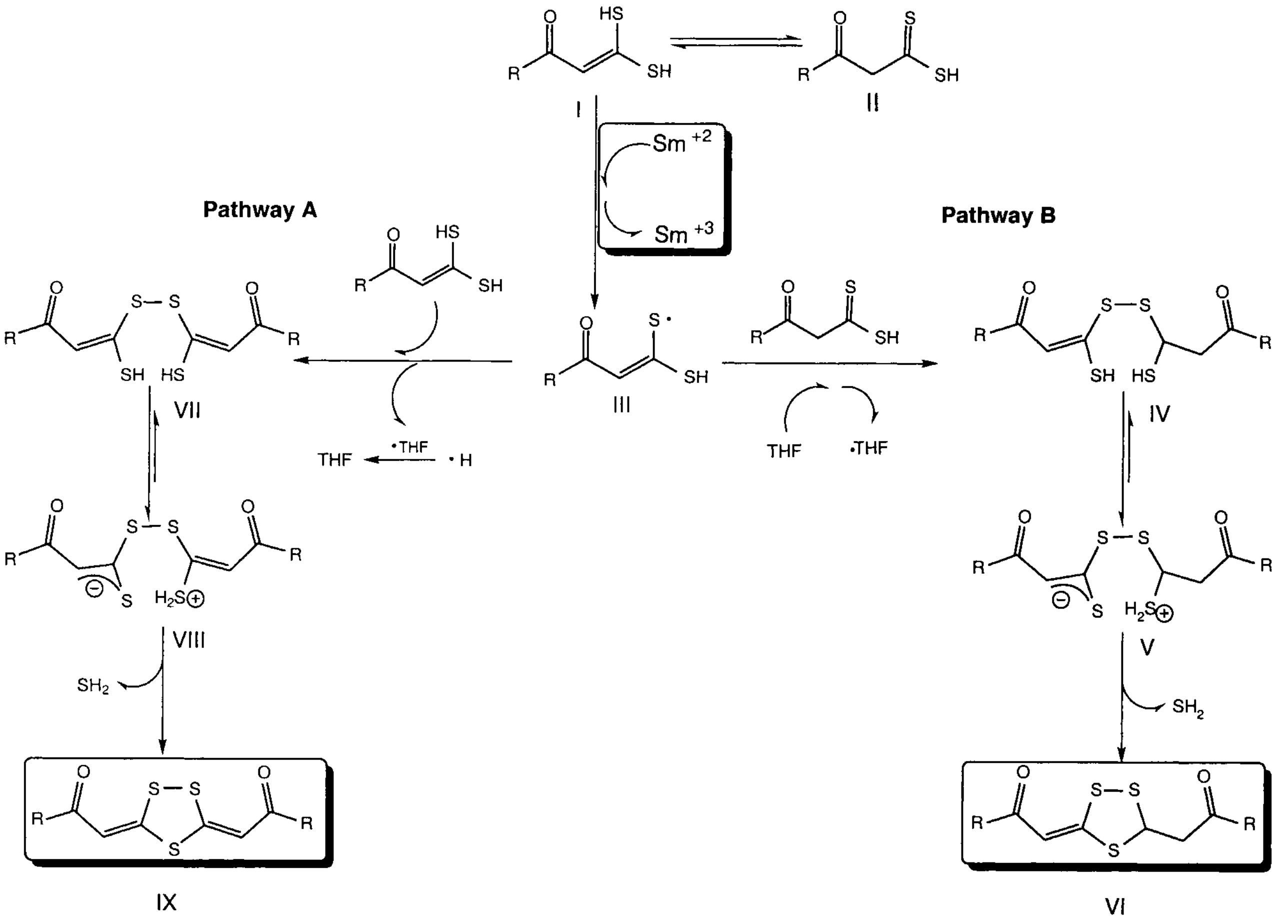
We report a novel SmI_2-mediated synthesis of 1,2,4-trithiole derivatives **2a–e** carried out, under very mild conditions, for the first time. The low diastero- and chemio-control found in this reaction suggests a noncoordinative substrate pathway in the samarium sphere. Work is in progress to increase the scope of our method, and attempts to increase the applications of these compounds in the syntheses of metallic complexes are also underway.

EXPERIMENTAL

General Methods

All NMR spectra were recorded on a Varian Unity 500 MHz spectometer (500 MHz for ^{1}H and 125.7 MHz for ^{13}C) at a probe temperature of 25°C. Reported peaks are referenced to internal TMS. All normal mode ^{13}C NMR spectra were acquired with composite pulse decoupling, namely a wide-band alternating-phase lower-power technique for zero residue splitting (Waltz 16) as implemented in the spectrometer software. The sequence for the inverse mode HMBC includes a low-pass J filtration [13] to suppress one bond correlation (evolution time: 3.6 ms). The polarization transfer time was set to 90 ms to optimize for long-range heterodecoupling. The recycling delay was 2.5 s. A total of 128 2K point spectra were acquired and zero-filled to 256 in t_1 window functions, including a shift by $\pi/6$ in t_2 and 2 Hz Lorentzian broadening in t_1 dimensions. The IR spectra were recorded on a Perkin-Elmer 283 B or 1420 spectrometer. The electronic impact (EI) ionization mass spectra were acquired on a JEOL JMS-SX102-A mass spectrometer operated in the positive-ion mode. The acquisition conditions were: ion source temperature, 230°C; ionization energy, 70 eV; and ionization current, 100 μA. Melting points were measured using a Mel-Temp II apparatus and are uncorrected. Column chromatography was performed with Merck silica-gel (70–230 mesh) using hexane/ethyl acetate in a 9:1 ratio as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under a nitrogen atmosphere in carefully dried glassware. Tetrahydrofuran (THF) and *o*-xylene were distilled from sodium-benzophenone under an argon atmosphere.

Synthesis of the Benzoyldithioacetic Acid Derivatives **1a–e**. A solution of sodium *tert*-amylate (0.2 mol) in *o*-xylene under magnetic stirring was allowed to react with the ring-substituted acetophenone (0.1 mol) and carbon disulfide (0.2 mol) for 12 hours. The reaction mixture was extracted twice with water (50 mL), and 10% H_2SO_4 was added. The precipitate was filtered off and washed with *n*-hexane, giving the corresponding products with yields ranging from 46 to 80%.



SCHEME 2

Reductive Coupling of Benzoyldithioacetic Acid Derivatives **2a–e** *Mediated by SmI*$_2$. To a solution of Sml2 in THF (0.1 mol) was added the benzoyldithioacetic acid derivative (0.1 mol) under a nitrogen atmosphere and with magnetic stirring over a period of 10 to 15 min. Then, the solvent was removed in vacuo and the residue was chromatographed on silica-gel; elution was performed with hexane/AcOEt in varying ratios to obtain the corresponding products **2a–e**.

3-(4-methoxyacetobenzophenyliden)-5(4-methoxyacetobenzophenyl)-1,2,4-trithiole **2a**. (0.87 g, 47%), m.p.: 162 °C; IR ν_{max} (KBr)/cm^{-1}: 1666.8 (C=O), 1600 (C=O), 1455 (C=C), 1256 (C-O), 1231 (C-O), 1027 (CS_2), 602.3 (C-S); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.86 (s, 3H, $OC\underline{H}_3$), 3.87 (s, 3H, $OC\underline{H}_3$), 3.65 (dd, 1H, H-13, J_{34} = 18, J_{32} = 7.5), 3.77 (dd, 1H, H13′, J_{43} = 18, J_{42} = 6.5), 5.44 (dd, 1H, H-5, J_{23} = 7.5, J_{24} = 6.5), 7.52 (s, 1H, H-6), 6.93 (m, 1H, H-17,17′), 6.95 (m, 1H, H-10,10′), 7.91 (m, 1H, H-16,16′), 7.95 (m, 1H, H-9,9′); ^{13}C NMR (125 MHz, $CDCl_3$): δ 44.0, 52.3, 55.6, 55.6, 109.9, 114.0, 129.0, 129.7, 130.3, 130.5, 163.3, 164.2, 168.1, 184.9, 194.3 (C-13, C-5, C-12, C-19, C-6, C-17, 17′, C-15, C-8, C-9, C-16, C-18, C-11, C-3, C-7, C-14); MS-EI (70 eV) *m/z* (% a.r.): 416 (10%)[$M^{+\bullet}$], 283 (18%) [$M-C_8H_7O_2$], 224 (8%)[$M-C_{10}H_9O_2S$], 193 (17%)[$M-C_{10}H_9O_2S_2$], 135 (100%)[$M-C_{12}H_{11}O_2S_3$].

s-cis-Bis[(2-methoxy)acetobenzophenyliden]-1,2,4-trithiole **2b**. (0.74 g, 40%) m.p.: 194–196°C; IR ν_{max} (KBr)/cm^{-1}: 1589*m* (C=O), 1481 (C=C), 1212 (C-O), 1017 (CS_2), 625 (C-S); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.92 (s, 6H, $-OC\underline{H}_3$), 7.60 (s, 2H, H-6), 6.98 (d, 2H, H-10), 7.05 (ddd, 2H, H-12), 7.48 (ddd, 2H, H-11), 7.86 (dd, 2H, H-13); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.7, 111.7, 12.7, 121.0, 126.6, 131.5, 133.7, 158.4, 158.7, 185.1 (C-10, C-6, C-12, C-8, C-13, C-11, C-3, C-9, C=O); MS-EI (70 eV) *m/z* (% a.r.): 416 (13%)[$M^{+\bullet}$]; 224 (8%)[$M-C_{10}H_8O_2S$]; 135 (100%)[$M-C_{12}H_9O_2S_3$].

s-trans-Bis-[(2-methoxy)acetobenzophenyliden]-1,2,4-trithiole **2b**. (0.80 g, 43%) m.p.: 156–158°C; IR

ν_{max} (KBr)/cm^{-1}: 1585.9*m* (C=O), 1560 (C=O), 1463 (C=C), 1441 (C=C), 1209 (C-O), 1035*d* (CS_2), 623 (C-S); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.92 (, s, 3H, H-14), 3.92 (s, 3H, H-23), 7.57 (s, 1H, H-6), 7.87 (s, 1H, H-15), 7.0 (d, 2H, H-10), 6.98 (d, 1H, H-19), 7.05 (ddd, 2H, H-12), 7.04 (ddd, 2H, H-21), 7.50 (ddd, 2H, H-11), 7.48 (ddd, 1H, H-20), 7.95 (dd, 1H, H-13), 7.80 (dd, 1H, H-22); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.7, 55.6, 111.7, 111.7, 113.1, 114.6, 121.0, 121.0, 125.4, 127.4, 131.6, 131.4, 133.6, 134.0, 158.7, 158.4, 168.6, 185.3, 157.4, 185.1(C-14, C-23, C-10, C-19 C-6 C-15, C-21, C-12, C-8, C-17, C-13, C-22, C-11, C-20, C-9, C-18, C-3, C-13, C-16, C-5); MS (EI) (70 eV) *m/z* (% a.r.): 416 (8%)[$M^{+\bullet}$]; 224 (6%)[$M-C_{10}H_8O_2S$]; 135 (100%)[$M-C_{12}H_9O_2S_3$].

s-cis-Bis[(3-methoxy)acetobenzophenyliden]-1,2,4-trithiole **2c**. (0.85 g, 46%), m.p.: 196–198°C IR ν_{max} (KBr)/cm^{-1}: 1573 (C=O), 1466 (C=C), 1265 (C-O), 1207 (C-S), 1035 (CS_2), 609 (C-S); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.88 (s, 6H, $-OC\underline{H}_3$), 7.47 (s, 2H, H-6), 7.11 (d, 2H, H-11), 7.39 (ddd, 2H, H-1), 7.52 (ddd, 2H, H-9), 7.53 (dd, 2H, H-13); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 112.4, 107.9, 119.5, 120.3, 129.7, 137.8, 160.1, 160.1, 185.0 ($-O\underline{C}H_3$, C-9, C-6, C-11, C-13, C-12 C-8 C-3,5, C-10, $C=\underline{O}$); MS-EI (70 eV) *m/z* (% a.r.): 416 (22%)[$M^{+\bullet}$]; 224 (6%)[$M-C_{10}H_8O_2S$]; 135 (100%)[$M-C_{12}H_9O_2S_3$].

s-trans-Bis[(4-methyl)acetobenzophenyliden]-1,2,4-trithiole **2d**. (0.73 g, 43%), m.p.: 205 dec; 235 funde. IR ν_{max} (KBr)/cm^{-1}: 1599 (C=O), 1451 (C=C), 1235 (C-O), 1058 (CS_2), 580 (C-S); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (H-6); 7.62 (H-13); 7.87 (H-9,9′), 7.30 (H-10,10′), 3.92 (H-12,19); ^{13}C NMR (125 MHz, $CDCl_3$): 185, 143.7, 134, 129.5, 128.2, 159.6, 107.8, 21.7 (C=O, C-11, C-10, C-9, C-8, C-3,5, C-6, C-12,19); MS-EI (70 eV) *m/z* (% a.r.): 384 (26%)[$M^{+\bullet}$]; 208 (14%)[$M-C_{10}H_8OS$]; 119 (100%)[$M-C_{12}H_9OS_3$].

s-cis-Bis[(4-methyl)acetobenzophenyliden]-1,2,4-trithiole **2d′**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (H-10,10′), 7.46 (H-6); 7.28 (H-9,9′), 2.42 (H-12).

s-trans-Bis[(4-fluoro) acetobenzophenyliden]-1,2,4-trithiole **2e**. (0.55 g, 30%), m.p.: 260; IR ν_{max} (KBr)/cm^{-1}: 1598 (C=O), 1567 (C=O), 1450 (C=C), 1223 (C-O) 1056, 592 (C-S); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6 (s, 2H, H-6), 7.4 (s, 2H, H-12), 8.0 (m, 4H, H-9,9′), 7.2 (m, 4H, H-10,10′); ^{13}C NMR (125 MHz, $CDCl_3$): δ 211, 171, 167, 163, 129.4, 129.3, 116.4, 116.1, 107 (C-7, 13, C-3,5 C-11, C-8, C-9,9′, C-10,10′, C-15,15′, C-16,16, C-6,12); MS-EI (70 eV) *m/z* (% a.r.): 392 (16%)[$M^{+\bullet}$]; 212 (13%)[$M-C_9H_5OSF$]; 123 (100%)[$M-C_{11}H_6OS_3F$].

X-ray Crystal Structure Determinations of Compound **2a**

Suitable crystals of **2a** were obtained as yellow plates from a mixture of CH_3OH/CH_2Cl_2 (2:1). The data mounted crystal was of approximate dimensions: 0.24 × 0.20 × 0.02 mm. The data were collected at 20° on a Siemens P4 diffractometer equipped with graphite monochromated CuKα radiation (λ = 1.54178 Å). Details of crystal data, data collection, and structure refinement are listed in Table 2. Three reflections (2 0 −4; 2 0 −6; 1 1 −2) were measured every 97 reflections to monitor the instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 0.989 to 1.00. The data were corrected for Lorentz-polarization and an empirical absorption correction based on the face-indexed method was also applied. The structure was solved by direct methods [14] and refined by full-matrix least-squares on F^2 [15] with anisotropic thermal parameters for the non-hydrogen atoms (Table 3). All the hydrogen atoms were included as fixed contributions and not refined. Their idealized positions were generated from the geometries about the attached carbon atoms and forced to ride on it with a fixed isotropic temperature factor, $U = 1.2$ times the U_{eq} of the parent C-atom and C-H distance of 0.96Å. The quantity minimized during the least-squares analysis was $(w\ F_o^2 - F_c^2)^2$, with $w = 1/[\sigma^2(F_o^2) + (0.0265P)^2]$, where $P = (F_o^2 + 2Fc^2)/3$. Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number CCDC 144414.

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